POLYMER COATED WEB WITH GOOD WATER VAPOUR PERMEABILITY

Field of the invention.

The present invention relates to a composite material, especially a laminate material, that comprises a substrate layer and a coating layer that comprises a plastics material. The invention relates, especially to such a composite material that is permeable to water vapour and can be used as or in a wall covering.

Background to the invention.

Many uses exist for water-vapour-permeable composite materials which have a degree of water resistance. Typical applications include diaper cover sheets, 'breathable' clothing, wrapping for prefabricated building components, wallcoverings and medical drapes and gowns. Many constructions of such composites have been proposed, usually comprising a paper, nonwoven or textile substrate which is coated with a polymeric film that has been processed to enable that film to be water-vapour permeable. One method is to form the film, then perforate it and laminate it to the substrate web; this is a complex process involving several steps. US-A-5 089 075 (Sonada), however, describes a extrusion laminating process in which the cooling roll has a modified surface that perforates the film.

Other methods employ means for providing discontinuities in the polymeric film so that if the film is stretched then pores are created. Typically, the discontinuities are created by incorporating mineral fillers into the polymeric composition before film forming. A method of forming such films is described in EP-A-0 605 831 (Yamamoto et al, assigned to Mitsubishi Petrochemical Co. Ltd.). Also, WO-A-97/29909 (Wu et al, assigned to Clopay Plastic Products Co., Inc.) describes a process in which a thermoplastic film containing pore forming fillers is extrusion coated onto a nonwoven and then stretched. These methods all require the film or composite to be stretched (various other methods of carrying out the stretching can be found in the prior art) after coating, creating an extra stage in the process.

US-A-5 262 444 (Rusincovitch et al) describes a method for the production of a wall covering in which a low boiling point additive (e.g. water) is added to a plastisol comprising a curable plastic and a plasticiser before extrusion of the plastisol onto a substrate, e.g. paper. The resultant coating is then cured under conditions such that the low- boiling point additive vaporizes and creates voids in the film.

In GB-A-2 271 519 (Kano, assigned to Toyokasei Co. Ltd.) there is described a means of creating a permeable layer in a composite product. In this case particulate

materials are incorporated into a polymeric resin which is applied to a nonwoven using an automatic spray gun or painting robot. This process produces a relatively thick coating, is relatively slow and the use of spray application methods will often result in an uneven coating.

EP-B-734,321 (Kimberly-Clark Worldwide Inc.) discloses a laminate that comprises a film formed from a blend containing, on a dry weight basis relative to the total weight of the film, from 10 to 68% of a predominantly linear polyolefin polymer, for example a linear low-density polyethylene; from 30 to 80% of a filler, for example calcium carbonate, generally having an average particle size of from 0.1 to 7 μm; and from 2 to 20% of a bonding or tackifying agent, which may be selected, for example, from various hydrogenated hydrocarbon resins, petroleum hydrocarbon resins, polyterpene resins, ethylene-propylene rubber (EPR) and olefinic thermoplastic polymers in which EPR is dispersed in polypropylene or a polypropylene/polyethylene blend. Once the film has been formed, it is stretched in order to render it porous and breathable; in particular, the film should have a water vapour transmission rate of at least 100 $g/m^2/24$ h. The stretched film is then bonded to a fibrous polyolefin nonwoven web, for example a spun bonded polypropylene web. The bonding of the film to the web may be effected by thermal bonding, in particular by using heat and pressure as with heated, patterned bonding rolls or using ultrasonic bonding means. It is suggested that the bonding agent can alternatively be added to the fibrous nonwoven web. The laminate may find use as a replacement for plastic films used as backing sheets in such absorbent products as diapers.

WO-A-98/02609 (Kimberly-Clark Worldwide Inc.) discloses a reinforced film comprising a film layer that is oriented in a direction of stretching and that has an effective gauge of 0.6 mil (15.24 μm) or less. The film layer is formed from a blend including, on a weight basis relative to the total weight of the film layer, from 30 to 70% of a polyolefin polymer, from 70% to 30% of a filler and, optionally, up to 20% of a second polyolefin polymer, the film layer having a water vapour transmission rate of at least 300 $g/m^2/24$ h. A pattern of adhesive areas is applied to a surface of the film layer, these adhesive areas having an add-on amount of from 0.1 to 20 g/m^2, a percentage bond area of from 5% to 50% per unit area of said surface, and a maximum spacing between adhesive areas, in a direction generally parallel to the said direction of stretching, of 1 inch (25.4 mm) or less. A suitable polyolefin polymer is linear low-density polyethylene. A suitable filler is calcium carbonate, which may be coated with stearic acid. The adhesive may, for example,

be a conventional hot melt adhesive, pressure sensitive adhesive or reactive adhesive; block copolymer-type construction adhesives, ethylene vinyl acetate-based adhesives and amorphous alpha-olefin copolymer and terpolymer-based adhesives are mentioned. Although the primary function of the pattern of adhesive areas is to reinforce the film layer, the adhesive can be selected so that it remains tacky for a sufficient period of time to allow it to bond the surface of the film layer to a surface of an adjacent layer such as a nonwoven web or fabric. The film may find use as an outer cover in personal care absorbent articles such as diapers.

A commonly used type of wallcovering is the so-called 'vinyl' wallpaper which is normally a polyvinyl chloride (PVC) plastisol coated paper. Though this material can be used for a wide range of wallcovering applications, it is particularly used in areas where good durability and washability are required in both residential and commercial applications. However, the use of PVC does create some problems: in the coating and subsequent printing process it is necessary to have emission control equipment and the wallcovering itself is not flame retardent and emits hydrochloric acid and dense smoke when exposed to flame. When based on paper, the wall covering is not particularly dimensionally stable nor is it strippable when redecoration is carried out.

In the wallcover market, concerns have also been expressed regarding the impact of the use of PVC on the environment and on health, motivating the search for alternative materials.

It could be imagined that other polymer coatings might overcome these problems but such coatings have a major disadvantage themselves; they have a very low water vapour permeability (WVP), which may be measured as the water vapour transmission rate (WVTR). Thus, when the wallcover is hung using water-based adhesives, which is the common method, the wallcovering is very slow to dry and is subsequently prone to mould growth.

Summary of the invention.

The present invention, in one of its aspects, now provides a composite material comprising a substrate layer and a coating layer, characterised in that the coating layer comprises a plastics material, which plastics material is selected from olefin polymers, olefin copolymers, blends of olefin (co)polymers and mixtures of two or more of these, the said plastics material having particles of filler therein. In general, the composite material is permeable to water vapour. In general, the said substrate layer and the said coating layer

are each permeable to water vapour. In certain embodiments no further layer is included; however, in other embodiments, any additional layer will generally also be permeable to water vapour.

The present invention, in another aspect, also provides a process for the production of a composite material, which process comprises applying a coating formulation as a coating layer on a substrate layer, the coating layer and substrate layer being permeable to water vapour, wherein the coating formulation comprises a plastics material that is selected from olefin polymers, olefin copolymers, blends of olefin (co)polymers and mixtures of two or more thereof and has particles of filler therein.

The present invention, in yet another aspect, also provides a coating formulation that comprises a plastics material that is selected from olefin polymers, olefin copolymers, blends of olefin (co)polymers and mixtures of two or more thereof and that has particles of filler therein. The coating formulation may, of course, contain one or more other components: in certain preferred embodiments, however, it consists essentially of the plastics material and the filler. The filler may be a single material or a mixture of different materials.

In further aspects, the present invention also provides the use of the said composite material as a wall covering. Thus, the invention provides the said composite material for use as a wall cover material and also provides a method of covering a wall surface that comprises applying to it a composite material of this invention.

Description of exemplary embodiments of the invention.

When the substrate of the composite is a nonwoven, it is preferably wetlaid. Nonwovens used as the substrates will generally comprise natural, in particular cellulose, fibres and/or synthetic fibres, the latter expression including fibres of organic polymers or copolymers such as polyesters. Thus, the nonwovens can comprise woodpulp fibres, preferably both softwood and hardwood pulp fibres, and short cut polyester fibres. Additionally a filler, especially calcium carbonate, is preferably incorporated in the web to provide high opacity. The nonwoven can be bonded with a resin binder formulation, especially an acrylic or vinyl acetate resin formulation. The fibre length and linear density of the polyester fibres should be chosen to give good web uniformity and will, typically, be in the range 5 to 20 mm and 1.0 to 6.0 denier (9 to 54 tex) respectively. The woodpulps should be chosen to provide a good combination of strength, opacity and coating performance; their choice should preferably also recognise current environmental concerns.

Typical formulations for the nonwoven are 20 to 40% pulp (preferably 10 to 20% softwood pulp, 10 to 20% hardwood pulp), 10 to 20% synthetic (preferably polyester) fibre, 25 to 35% calcium carbonate, the percentages being by weight of the nonwoven on a dry weight basis, the remainder preferably comprising a binder. The binder should preferably be applied though a spray application or size press and preferably at a level to give between 15 to 20% solids in the finished substrate. The grammage (basis weight) of the substrate is preferably in the range 30 to 200 g/m^2. The substrate will, in certain preferred embodiments, have a thickness of from 40 to 500 μm, more preferably at least 80 μm, for example up to 300 μm.

Other substrates include papers, e.g. papers that are conventionally used as wallcovering substrates, and spunbonded, SMS and hydroentangled nonwovens. ("SMS" is a conventional acronym for a nonwoven composite comprising layers of spunbonded (S), melt blown (M) and spunbonded (S) webs.) Paper substrates may be exemplified by "Cresta Print M" and "Cresta Print F1" from Metsä-Serla Paperboard. ("Cresta" is understood to be a registered trade mark.)

The plastics material (which expression herein includes synthetic resins and synthetic polymeric materials) is preferably a polymer or copolymer of a C_2-C_4 olefin, especially of ethylene or propylene, or a blend comprising such a polymer or copolymer. Suitable co-monomers are C_1-C_4 alkyl acrylates or C_1-C_4 alkyl methacrylates. A particularly preferred plastics material is a copolymer of ethylene and n-butyl acrylate; such copolymers are described by L.K. Johnson, "Ethylene n-Butyl Acrylate Copolymers for Extrusion Coating and Lamination Applications", *Polymers, Lamination and Coatings*, a TAPPI PRESS Anthology of Published Papers, 1986-1991, pages 248-252.

Preferably, the plastics material has a water vapour transmission rate of at least 14 g/m^2 per 24 h at 25°C/75% RH (relative humidity) as measured on the unfilled plastics material at a mass per unit area of 45 g/m^2. The composite comprising the substrate layer and the coating of filled plastics material preferably has a water vapour transmission rate of at least 30 g/m^2 per 24 h at 25°C/75% RH.

The particulate filler distributed or dispersed (preferably uniformly distributed or dispersed) in the plastics material is preferably a mineral or inorganic filler, especially calcium carbonate and/or titanium dioxide. Other mineral fillers may come into consideration, e.g. talc, kaolinite, alumina trihydrate, feldspar or silica. Typical particle sizes of the fillers are in the range of from 0.1 to 10 μm, e.g. from 0.5 to 7 μm.

In general, the amount of particulate filler will be 40% or less, relative to the weight of filled plastics material: preferably the amount of filler will be 35% or less, more preferably 30% or less. In general, the mineral filler will be used in an amount effective to achieve a good water vapour permeability. Usually, the amount of mineral filler in the filled plastics material will be 2% or more, preferably at least 5%, more preferably 10% or more and most preferably at least 20% by weight.

Typical formulations for the plastics material are mixtures or alloys of an ethylene butyl acrylate copolymer (EBA) comprising 60 to 70% EBA, 20 to 30% calcium carbonate and 5 to 10% titanium dioxide, percentages being by weight of the mixture or alloy. Typically the basis weight (grammage) of the polymer layer is from 5 to 50 g/m^2, preferably from 10 to 50 g/m^2.

The plastics material can be applied to the substrate by any appropriate coating method. Extrusion is the preferred method, for example conventional flat die extrusion. Extrusion coating techniques are well known: see for example, Modern Plastics Encyclopaedia 1980-1981, McGraw-Hill Inc. pp 253-256. Moreover, other methods, such as knife coating, roll coating or transfer coating may come into consideration.

In certain preferred embodiments the coating layer will have a thickness of from 10 to 50 μm, e.g. from 25 to 50 μm.

A preferred embodiment of the invention comprises a wetlaid nonwoven web formed from woodpulp and polyester fibres into which is incorporated calcium carbonate bonded with resin. This nonwoven web is then extrusion coated with a polymer layer consisting of ethylene butyl acrylate, calcium carbonate and titanium dioxide.

In a particular application of the invention, a composite nonwoven is used as a base for a wallcovering which can be embossed and/or printed to give the required decorative effects. A nonwoven web, extrusion coated with a polymer, copolymer or polymer alloy, according to the invention will have many advantages over the prior art and overcomes a major problem with many other extrusion coated materials in that the material of the invention is permeable to moisture vapour so that drying of the hung wallcovering is not impeded.

The advantages of the composite nonwoven compared with the prior art, particularly the polyvinyl chloride coated papers, are that:

the composite nonwoven is fast drying and, because it is breathable, mould growth is eliminated;

since the composite is PVC free, there is no need for emission control equipment to be installed at the extrusion coating process nor in the subsequent printing processes; it is also odourless in use;

the composite has a smooth surface so that it has good rotogravure printability; it is also hot or cold embossable;

the coating layer can be applied in a thickness conventionally accepted in the wall cover art, that is to say excessively thick layers are not required;

adequate permeability may be achieved without the need for the addition of special low-boiling point additives, such as water or blowing agents;

the composite is flame retardent and there is no smoke release on burning;

the composite is dimensionally stable so that there is no seam separation and paper-based complexes are more dimensionally stable than those of the prior art;

hanging of the wallcover is facilitated by the good lay-flat properties, ease of cutting and strippability;

following the extrusion step and, if required, a curing step, there is no need for an additional processing step; in particular there is no need for a special stretching step in order to achieve the requisite permeability to water vapour. In certain preferred embodiments the composite material during its manufacture is not subjected to any substantial stretching, in either the machine direction (MD) or the cross direction (CD). Thus, in each of said directions, the composite material will normally be stretched by not more than 3 percent, preferably by not more than 2 percent, more preferably by not more than 1 percent, and most preferably there is essentially no stretching. Accordingly, the manufacturing equipment will generally be run at zero MD stretch and with no applied CD stretch. It is not precluded that in certain embodiments some shrinkage might occur in at least one direction.

The composite or laminate materials of the present invention will also come into consideration for other uses, for example in medical drape and gown materials.

Test methods.

Grammage: ISO 536

Appearance: A visual assessment against standard samples;

1 = unacceptable

2 = accepted with major remarks.

3 = accepted with minor remarks.

4 = totally acceptable.

Curl: Measured in mm. deviation from a flat surface after making an X-cut with the arms of the X being 160 mm long and at 45° to the machine direction.

Pinholes: Bendtsen porosity measured according to ISO 8971-4 after the sample is treated at 150°C for one minute. If there is zero porosity "OK" is reported.

Water vapour transmission rate (WVTR), measured according to DIN 53122, expressed as g/m^2 per 24hrs at 25°C and 75% RH.

Opacity: Elrepho %, measured according to SCAN P-3: 75.

Fire rating and smoke intensity: SIS 02 48 23.

Nicotine stain: degree of yellowing when subject to tobacco smoke expressed as the % increase in the b value of the L a b colour measurements.

Dimensional stability: the % increase in length in the cross direction after 10 minutes of a 100 mm square sample pasted to a plaster board surface.

Strippability: the % of the sample remaining on a plaster board substrate after an attempt to pull the sample off 14 days after it had been pasted to the substrate.

Examples.

The invention is illustrated by means of the following examples, in which reference is made to the above test methods.

Example 1.

A 70 g/m^2 nonwoven substrate comprising a fibre blend of 40% 1.7 denier (15.3 tex), 15 mm precision cut polyester fibre and 60% woodpulp bonded with a vinyl acetate resin binder such that the total fibre content was 80% and the binder content was 20%, was extrusion coated with 40 g/m^2 of a polymer alloy comprising 70% ethylene n-butyl acrylate copolymer (EBA) (Borealis grade 6417), 25% calcium carbonate (particle size 2 - 5 microns) and 5% titanium dioxide (particle size 2 - 5 microns). For the extrusion, the melt temperature was in the range 280 - 300°C and the length to diameter ratio for the screw was greater than 26.The test data are shown in Table 1.

Example 2.

This example is the same as Example 1 except that the extrusion coating was 30 g/m^2. The test data are again shown in Table 1.

Example 3.

The same substrate as in Example 1 was extrusion coated with 40 g/m^2 of a polymer alloy comprising 60% EBA, 30% calcium carbonate and 10% titanium dioxide. This

particular polymer alloy gave very inferior extrusion performance, probably because the filler content was too high. Test measurements were not made.

Table 1

Property	Example 1	Example 2
Grammage (g/m^2)	111	101
Delamination	No separation	No separation
Appearance	3	3
Curl MD	2-3	2-3
Curl CD	0	0
WVTR (g/m^2 per 24 hrs)	~50	~50
Elrepho opacity (%)	76.7	75.5

The test data demonstrate that materials made by the methods of Examples 1 and 2 provide good WVTR and can be produced with no difficulty using conventional extrusion coating processes. The opacity results were less than is normally required for wallcover applications so for this end use a substrate containing filler will commonly be required. An example with such a substrate is provided in Example 5.

Example 4.

Because the polymer compositions in Examples 1 and 2, based on EBA, gave such good results, evaluations of other polymers were carried out. In these cases the polymer blend contained no fillers and a 145 g/m^2 nonwoven substrate was used. (Though the grammage of the substrate was much higher than in the previous examples, it was very porous and would not have affected the WVTR results significantly.)

The extrusion coating coat weight was 45 g/m^2 and the polymers tested were:

Example 4a EBA (standard)

Example 4b Ethylene methyl acrylate (EMA)

Example 4c Low density polyethylene (LDPE)

Test data are included in Table 2.

Table 2

Property	Example 4a	Example 4b	Example 4c
Delamination	No separation	No separation	No separation
Appearance	4	4	4
Pinholes	OK	OK	OK
Water test	OK	OK	OK
WVTR (g/m² per 24 hrs)	14.2	8.8	1.9

This series of comparative tests of different polymers shows that EBA is to be preferred for high WVP. Comparison of Example 4a with Examples 1 and 2 demonstrates the synergistic effect of fillers on WVTR. The results also suggest that in order that a minimum WVTR of 30 g/m^2 per 24 hrs shall be achieved with a filled composition, the polymer itself should have a WVTR of 14 g/m^2 per 24 hrs at a mass per unit area of 45 g/m^2.

Example 5.

An 115 g/m^2 polyester/woodpulp nonwoven (Dexter grade 11877) was extrusion coated as in Example 2. Test data are included in Table 3 and compared with a typical prior-art vinyl coated product.

Table 3

	Example 5	Prior-art vinyl
Total grammage (g/m^2)	140	180
Fire rating	Class II	Class II
Smoke intensity	No smoke	8° max
WVTR (g/m^2 per 24 hrs)	30-70	25-55
Nicotine stain (%)	70	220
Dimensional stability (%)	0.07	0.78
Strippability (% release)	100	0
Elrepho opacity (%)	97	96

The overall superior performance of the example of the invention as a wall covering over that of the prior-art is clearly illustrated in the table.

It will, of course, be understood that the present invention has been described above purely by way of example and that modifications of detail can be made within the scope of the invention.